Novel electrochemical method of fast and reproducible fabrication of metallic nanoelectrodes

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Novel electrochemical method of fast and reproducible fabrication of metallic nanoelectrodes

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A novel electrochemical wire etching method of fabrication of ultrasharp nanoelectrodes is reported. Tungsten wires can be sharpened to less than 10 nm tip radius in a reproducible manner in less than 1 min by using controllable hydrodynamic electrolyte flow combined with optimized electrochemical etching parameters. The method relies on the variations of the electric field at the surface of a metal wire, while the electrolyte solution is in motion, rather than on the ionic gradient generated in a static solution. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4895639]

I. INTRODUCTION

Microprobes constitute very important tools when it is imperative to perform electrical or electrochemical operations in confined volumes of the microscale with minimum or no damage to the surrounding environment.

The fabrication of micro/nano probes has revolutionized the way research is done in various fields such as electroanalysis, biotechnology, medicine, imaging technology. The downsizing of metal wires to dimensions close to the atomic scale has enabled scientists to study micro- or even nano-scale volumes and greatly improve the ability to characterize such confined systems, whether the wires are used in their pure state or coated with another material.[1–5] Microelectrodes are the key elements that made possible the development of relatively new electrochemical techniques, such as SECM (Scanning Electrochemical Microscopy) and SVET (Scanning Vibrating Electrode Technique), or imaging ones such as STM (Scanning Tunneling Microscopy). Through the use of microelectrode based techniques it has been possible to acknowledge fast reactions of the order of microseconds or less or even detect species in concentrations as low as a few ppb.[6–10]

From all the different fabricating methods for microelectrodes, the electrochemical etching of a metal wire is widely used for single microelectrodes. Although the fabrication of micro- and nanoelectrodes has been reported by many research groups, the method by which they are produced is generally quite similar: a metal wire is immersed in an electrolyte solution, centered in a ring, coil, or tube, which work as the counter electrode (CE). Alternatively, the wire is passed through a lamellae of electrolyte solution held by surface tension to the surrounding CE ring. Upon applying a certain voltage, the ionic concentration gradient at the meniscus in contact with the wire leads to its sharpening, according to Eqs. (1) and (2) for the case of tungsten.[11–21]

$$\text{Cathode reaction}: \quad 6H_2O + 6e^- \rightarrow 3H_2\,(g) + 6OH^-, \tag{1}$$

$$\text{Anode reaction}: \quad W\,(s) + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e^-, \tag{2}$$

$$\text{Overall}: \quad W\,(s) + 2OH^- + 2H_2O \rightarrow WO_4^{2-} + 3H_2\,(g)\,.$$

Even though nanometric tip curvature radiuses and high aspect ratios can be obtained by such a procedure, it can be rather complex and the success rate for producing usable tips can be quite low in consequence of the many variables involved.[13,22]

Although the meniscus allows etching the wire to a pointed shape, many problems arise from using this configuration if extremely sharp tips are to be obtained in a reproducible manner. In a static configuration, the weight of the portion of wire below the etching zone strongly conditions the tip curvature radius. Moreover, if the system power is not turned off at the exact moment of the drop-of the sharp tip will become blunt due to over-etching.[21,23,24] Furthermore, the positioning of the wire during the etching is critical and has a determinant influence in the shape, size, and quality of the sharp tip. In fact, even slight vibrations, such as sound vibrations will affect the quality of the tips.[24] Avoiding these drawbacks might require a skilled operator and frequently the controlling systems are complex, because the current cut-off time strongly marks the difference between a good tip and a blunt tip.[13,25] Hence, although the existing electropolishing methods can provide metal tips with high quality, suitable for applications such as STM or AFM (Atomic Force Microscopy), the fabrication procedures tend to be highly sensitive to small modifications.

Here we report an alternative method in which the quality of the final tip depends exclusively on the parametric adjustment of all the components involved in the etching process does not require a fast or dedicated current cut-off circuit and allows the production of sharp metal nanotips in less than 1 min, in a reproducible manner.

II. EXPERIMENTAL

A simple method for the fabrication of a sharp micro/nanotip is described. This can be accomplished by the

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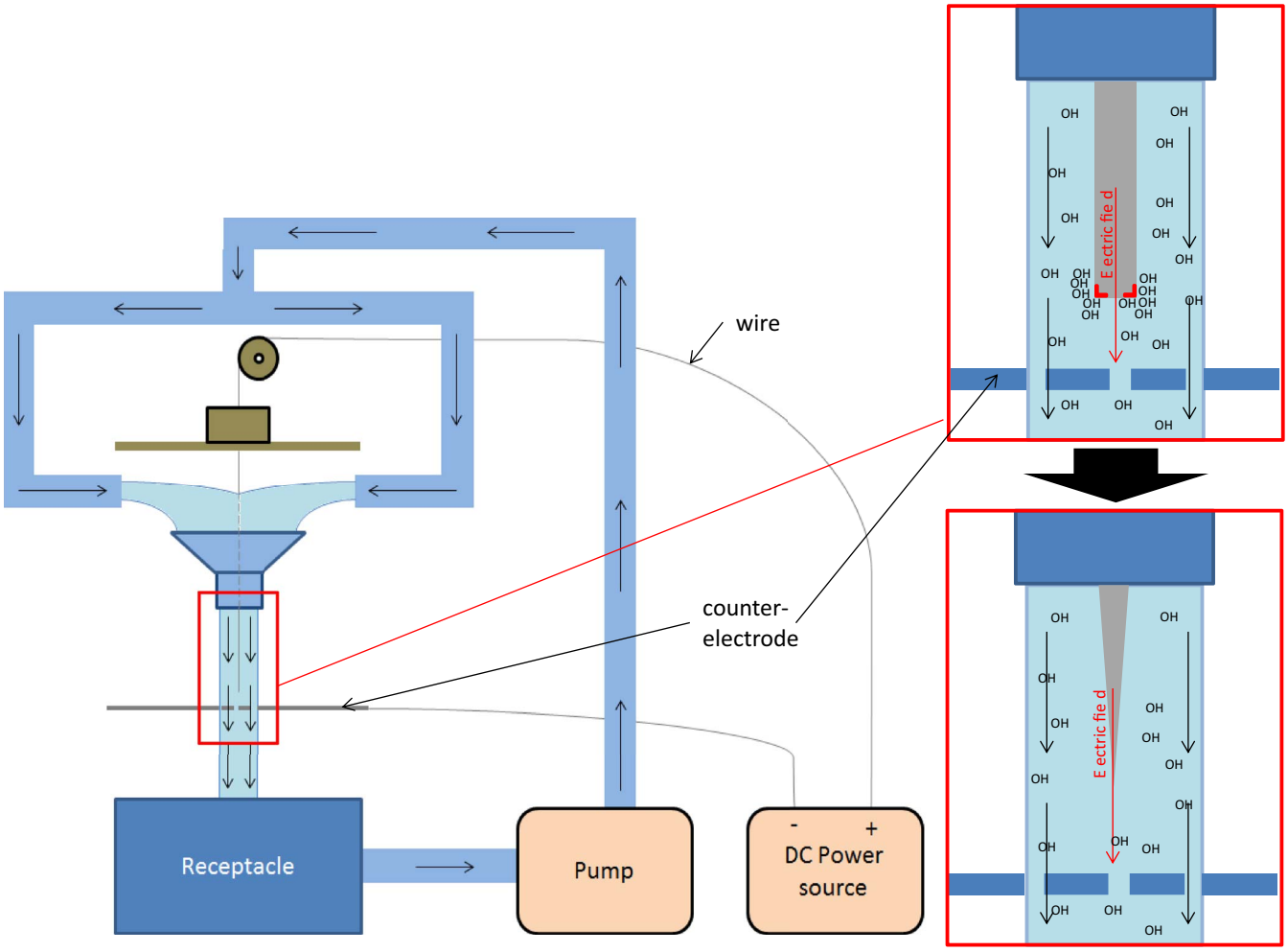

FIG. 1. Electrochemical etching assembly, evidencing the etching mechanism (inset).

assembly of a wire etching device comprising 3 main elements: (i) a DC power source for generating an etching voltage for metallic material removal from the wire and consequent wire sharpening; (ii) an etching unit constituted by the wire to be etched, a counter electrode and an electrolytic fluid which closes the circuit between the wire and the electrode, providing the necessary chemical species to react with the wire to be electropolished and the physical mean to transport the etched material; (iii) a pump and a flow circuit where the electrolyte fluid is made to flow in order to close the circuit on the etching unit (Fig. 1).

In this work, tungsten wires were used for demonstrating the performance of this novel electrochemical etching method. The counter electrode was also made of tungsten. Aqueous electrolyte solutions with various concentrations of NaOH from 0.5 to 4 M were used as etching fluid. A commercial pump (Boyu SP-700, China) with a flow capacity of 230l/h was used to provide the circular motion of the electrolyte solution. The constant flow of the electrolyte in a closed circuit has several advantages. The metal wire is not immersed in a static liquid, instead it is positioned in the center of a column of flowing electrolyte. By this system the electrochemical etching apparatus is greatly simplified and the shape, size, and quality of the metallic tips will be almost exclusively dependent on the electropolishing parameters and not on thorough operation details. The metal wire to be etched requires only to be aligned vertically at the center of the column of flowing electrolyte.

III. RESULTS AND DISCUSSION

A device integrating this new electrochemical etching method is depicted in Fig. 1. The essence of the method is the absence of meniscus formation. In this traditional approach the electrochemical etching occurs due to the OH^- ionic gradient that is formed at the meniscus between the metal wire and the electrolytic solution.

Instead, the suggested method is based on a reverse gradient compared to that observed at a meniscus. The etching procedure occurs in hydrodynamic conditions under an applied electric field. The ionic gradient driving the electrochemical etching occurs when voltage is applied to the system, as a consequence of the shape of the wire.

Taking a tungsten wire of 125 μm diameter and optimized parameters, this method can reproducibly deliver nanoelectrodes as sharp as 10 nm tip curvature radius or less with aspect ratio up to 15:1 (Figs. 2(a) and 2(b)) in less than 60 s (Fig. 2(c)). Accomplishing the fabrication of sharp tungsten

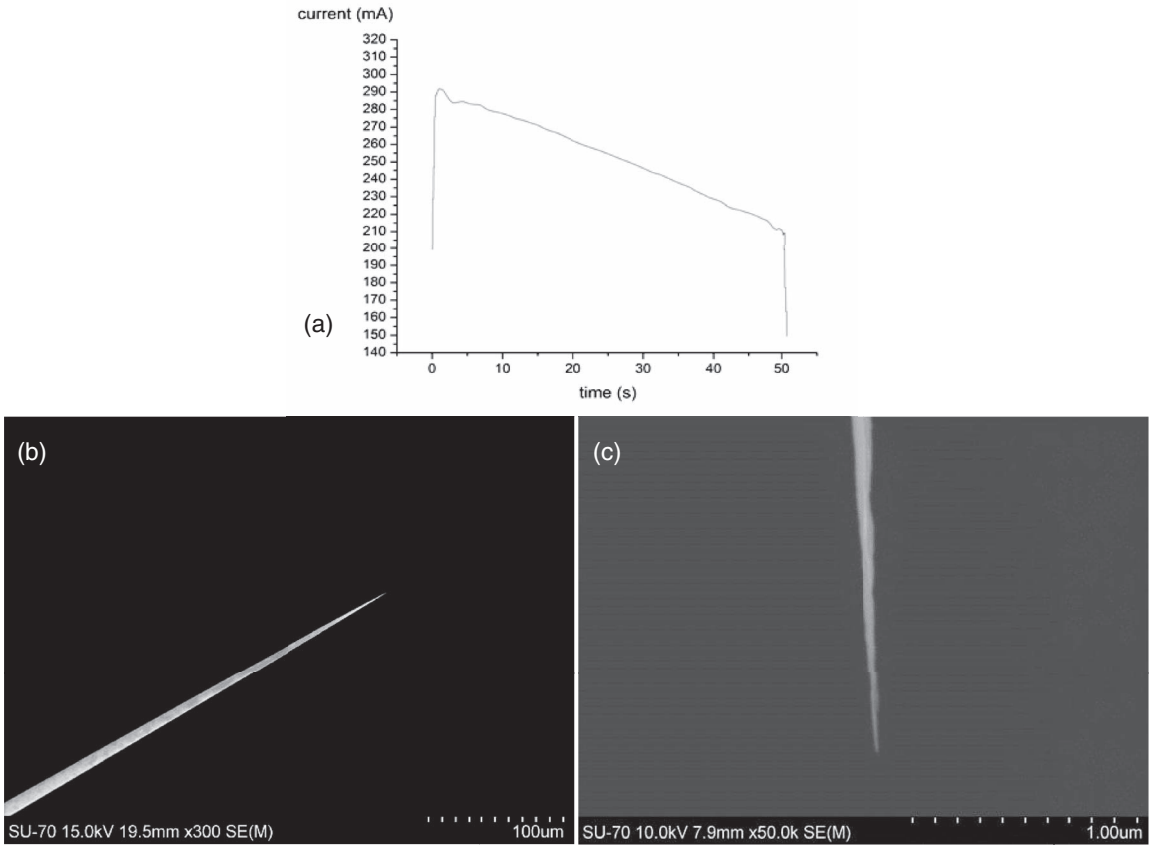

FIG. 2. Electrochemical etching process showing (a) current-time dependence using 1 M NaOH and 30 V applied on the DC power source, and electrochemically etched tungsten nanowire in (b) low magnification and (c) high magnification.

wires of the micrometer or the nanometer scale by the following uncomplicated procedure: (1) alignment of the metal wire until it is well centered with the collecting funnel and with the counter electrode bellow; (2) adjustment of the distance between the wire and the counter electrode; (3) turning on the pump to activate the flow motion of the electrolyte solution; (4) turning on the DC power source previously set to the desired voltage (say 30 V), during the desired amount of time (say 50 s); (5) turning off the power source; (6) cutting the needed part of the wire to be used as an ultrasharp electrode; (8) restarting from (1) for another electrode.

Since the method is based in a fluid in motion under the influence of an applied electric field, electrohydrodynamics must be considered. According to the Ohmic model, in the presence of a monovalent binary electrolyte which is fully dissociated with constant properties, the current density in a flowing electrolyte solution can be described by

$$J = QKE - D\nabla Q + Q\nu, \tag{3}$$

where Q is the charge density, K is the charge mobility, E is the electric field, D is the diffusion coefficient, ∇ is the gradient operator, and ν is the fluid velocity.[26]

The first term on the right side of the equation is the drift current of the free charges which move with a velocity $K\vec{E}$ relative to the fluid. The second term is the molecular diffusion, which can be considered negligible in comparison to the externally applied voltage (the thermal voltage is 25 mV at room temperature), and the third term is due to convection, which makes the charge to move with the fluid.[26]

TABLE I. Range of studied parameters used for electrochemical etching.

Electrolyte concentration (mol dm^{-3})	Applied voltage (V)	Wire-electrode distance (mm)	Wire diameter (μm)	Counter-electrode diameter (μm)	Etching time (s)
0.5	5	2	125	125	10
1	10	4	250	250	20
2	20	6		300	30
3	25	8		1000	40
4	30	10			50
	40	12			60
		14			70

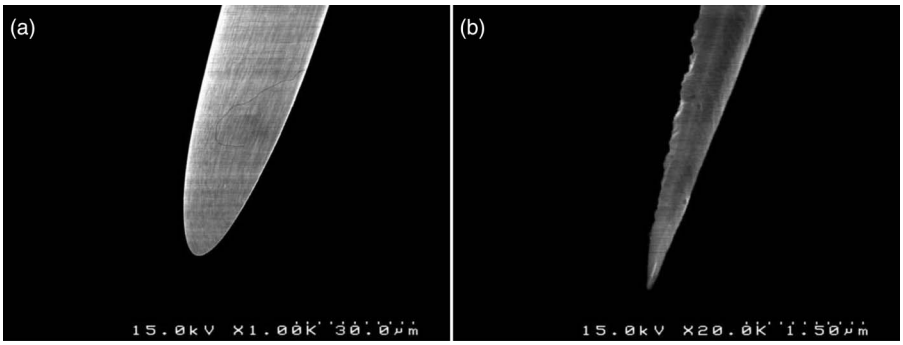

FIG. 3. Effect of electrolyte solution concentration on the shape and surface morphology of the etched tungsten wires, evidencing large tip curvature, and low aspect ratio with (a) 0.5 M NaOH and high surface roughness with (b) 4 M NaOH.

Considering the Coulomb force alone, the equations describing the electrohydrodynamic movement result from the combination of fluid dynamics (Eqs. (4) and (5)) and electrodynamics (Eqs. (6)–(8)),

$$\nabla \cdot \nu = 0, \tag{4}$$

$$\frac{\partial \nu}{\partial t} + (\vec{\nu} \cdot \nabla)\nu = -\frac{1}{\rho}\nabla p + \frac{\mu}{\rho}\nabla^2 \nu + \frac{QE}{\rho}, \tag{5}$$

$$\nabla \cdot E = \frac{Q}{\varepsilon}, \tag{6}$$

$$E = -\nabla \phi, \tag{7}$$

$$\frac{\partial Q}{\partial t} + (KE + \nu) \cdot \nabla Q = -\frac{KQ^2}{\varepsilon}, \tag{8}$$

where E is the electric field, Q is the charge density, ε is the permittivity, ϕ is the electric potential, $\vec{\nu}$ is the fluid velocity, ρ is the density, p is the pressure, μ is the viscosity, K is the charge mobility, t is the time, and ∇ is the gradient operator.

Equations (4) and (5) ignore the compressibility of the fluid and describe its movement taking into account the viscosity and the electric field. Equations (6)–(8) are the Maxwell equations accounting for the electrodynamics of charged molecules in the fluid.[26,27]

For perfect conductors (mercury, water) or perfect dielectrics (nonpolar liquids such as benzene), the electric stress is balanced by changes in the shape of the interface, and the Coulomb force is in the direction of the electric field.[28] Because low angle regions (e.g., edges, apexes) exhibit a higher density of electric field, they will be etched preferentially in relation to high angle regions. An auxiliary electrode positioned perpendicularly below the wire being electropolished, causes the shape of the resulting tip to be concordant with the vertical direction of the electric field.

Given the broad range of possible parametric combinations, a study was conducted based on the variation of each relevant parameter, regarding the device depicted in Fig. 1 (Table I).

A. Effect of electrolyte concentration, applied voltage, and wire-CE distance

Considering NaOH as a well-suited electrolyte for the electropolishing of tungsten wires, the effect of its concentration was studied in the range of 0.5–4 M.[29–31] The concentration of 1 M was considered to be optimal because it ensures a good balance between tip curvature radius and surface roughness. Lower concentrations contributed to a higher tip curvature radius and lower aspect ratio, while stronger electrolytes tend to yield higher surface roughness (Fig. 3).

Similar effects were found for the voltage applied between the wire and the counter electrode. A voltage of 30 V in the DC power source was considered to be optimal for the etching process. With lower voltage there is a tendency for the curvature radius of the tip to be larger, whereas with higher voltage the surface of the etched wire tends to exhibit higher roughness and higher number of imperfections (Fig. 4).

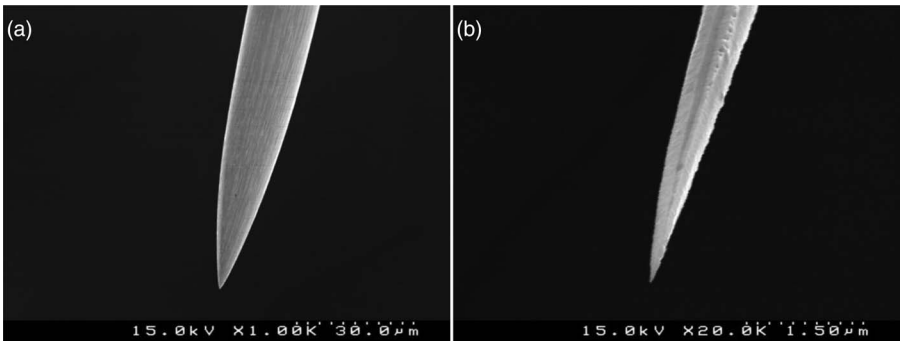

FIG. 4. Effect of applied voltage on the shape and surface morphology of the etched tungsten wires for (a) 5 V and (b) 40 V.

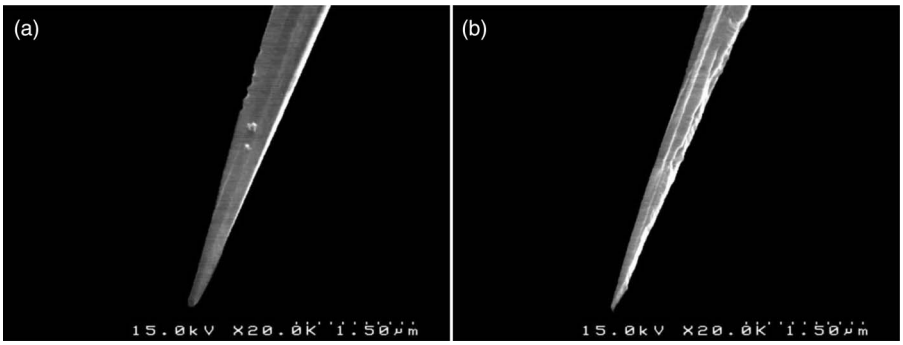

FIG. 5. Effect of the wire-counter electrode distance on the shape and morphology of the electrochemically etched tungsten wires for (a) 2 mm and (b) 14 mm.

The potential gradient determining the electric field (Eq. (7)) depended on the distance between the wire and the counter electrode. Distances of 2–14 mm between both were tested. A distance of ∼4 mm was found to provide the best results. Lower distances yield tips with larger curvature radius and higher distances will promote the appearance of a less smoother surface with possibly compromising defects (Fig. 5).

The electrolyte concentration, applied voltage, and wire-CE distance can be associated with the electric field characteristics by Eqs. (6)–(8). The variations in charge density and potential gradient induced by these parameters will determine the rate of metal removal occurring during the etching procedure. Moreover, the correlation of charge density with charge mobility and fluid velocity, considered in Eq. (8), can be used to relate the local progress of the anodic and cathodic reactions (Eqs. (1) and (2)) with the microstructural modifications occurring at the surface being etched, which will determine the balance between sharpness and roughness of the wires. Depending on the current density, metal removal from the surface of the wire can occur more selectively or more uniformly, for which the nomenclatures of etching and polishing have been ascribed, respectively. The selection of an adequate current regime is important in order to ensure that metal removal occurs homogeneously, avoiding the high energy regions (defects, grain boundaries) to be excessively attacked.[25]

B. Effect of etching time

Etching periods of 5–70 s were studied keeping the remaining conditions constant. Time is a very important variable because the electrochemical etching is preceded by the non-electrochemical dissolution of tungsten trioxide (WO_3),[25] which is the most stable tungsten oxide and is always present in a thin layer at the metal surface,

$$WO_3\,(s) + OH^- \rightarrow HWO_4^-\,(aq)\,, \tag{9}$$

$$HWO_4^-\,(aq) + OH^- \rightarrow WO_4^{2-}\,(aq) + H_2O. \tag{10}$$

The progression of this reaction can be seen in Figures 6(a) and 6(b), showing tungsten wires etched for 30 and 40 s, respectively, keeping all other parameters constant. In Fig. 4(a), after 30 s of etching the surface of the wire still presents a visible pattern resulting from the remaining oxide at the surface. After a few seconds, no oxide remains as it can be seen by the difference in the surface morphology shown in Figs. 6(a) and 6(b). Hence, after removal of most of the oxide at the surface of the wire the etching rate will be faster, as will be reduction in the wire length. The necessary etching time will also depend on the electrolyte concentration and the flow rate of the pump because they determine the instant concentration of OH^- available at the surface of the wire. From the third term of Eq. (3), it can be seen that higher fluid velocity will also yield higher current density. Considering a constancy of parameters during etching, varying these two parameters will also influence the quality and size of the tip. With 50s etching time, according to the conditions in Table II, the wire can be reproducibly sharpened down to a tip radius of less than 50 nm. Longer electropolishing periods do not implicate compromising the tip radius and tend to yield higher aspect ratio. An electropolishing time of 50 s was found to be optimal, considering that the rate of tips per hour is also important.

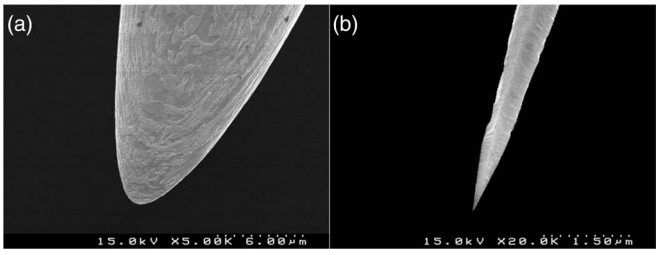

FIG. 6. Tungsten wires during etching in 1 M NaOH with 30 V applied voltage showing (a) oxide still present on the surface of the wire after 30 s; (b) wire without oxide after 10 extra-seconds of etching.

TABLE II. Optimized wire etching conditions, adequate for producing nanowires.

Electrolyte concentration (mol dm^{-3})	Applied voltage (V)	Wire-electrode distance (mm)	Wire diameter (μm)	Counter-electrode diameter (μm)	Etching time (s)
1	30	4	125	250	50
				300	
				1000	

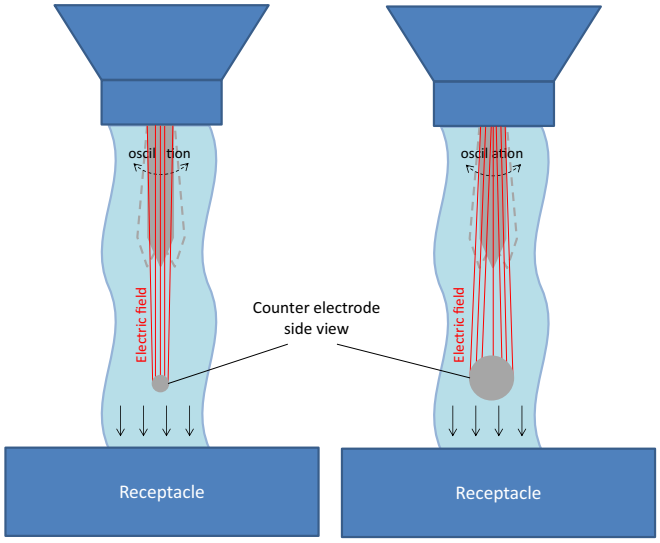

FIG. 7. Effect of counter electrode diameter: the electrical field between the wire and the counter electrode becomes increasingly more stable for larger CE diameters.

C. Effect of the auxiliary electrode diameters

The diameter of the auxiliary electrode was found to be perhaps the most critical parameter if tips of the nanoscale are to be produced reproducibly. The smaller the ratio between the diameters of the wire to be etched, d_w, and the counter-electrode, d_{ce}, the more reproducible becomes the fabrication of nanotips. We verified that by using a ratio $d_w/d_{ce} < 0.5$, more than 60% of the tips would exhibit a curvature radius with less than 50 nm. This is because the electric field becomes more stable. As the electrolyte solution flows, the wire will tend to oscillate, which causes instability of the electric field and the hydrodynamic regime. Considering a sufficiently wide column of flowing electrolyte, smaller d_w/d_{ce} ratios will reduce the probability of the wire oscillating outside the zone of action of the vertical electric field (Fig. 7).

The ratio between the diameter of the column of flowing electrolyte solution, d_{fes}, and the diameter of the counter electrode was found to be also important in the presented device configuration since as d_{ce} approaches d_{fes}, the electrolyte solution will tend to increasingly splash to the sides as it hits the counter electrode causing significant turbulences.

By adopting the conditions indicated in Table II, we have produced the nanosharp wires shown in Figures 8(a), 8(b), and 8(c) with counter electrode diameters of 250, 300, and 1000 μm, respectively.

Perhaps the best part of the method is depicted in Figure 9, where a collection of bad quality etched wires is shown, still exhibiting high aspect ratio and tip curvature in the 50–100 nm range.

Although this work was focused on the etching of tungsten wires, further applicability of this method may be found for metals forming a passive film, using electrolytes which lead to partial dissolution of this layer. As demonstrated this method can be implemented with very basic instrumentation and with either manual or automatic control. The applicability of sharp tungsten wires produced in this way has been demonstrated with CVD diamond coatings for scanning probe electrochemical measurements.[3,32]

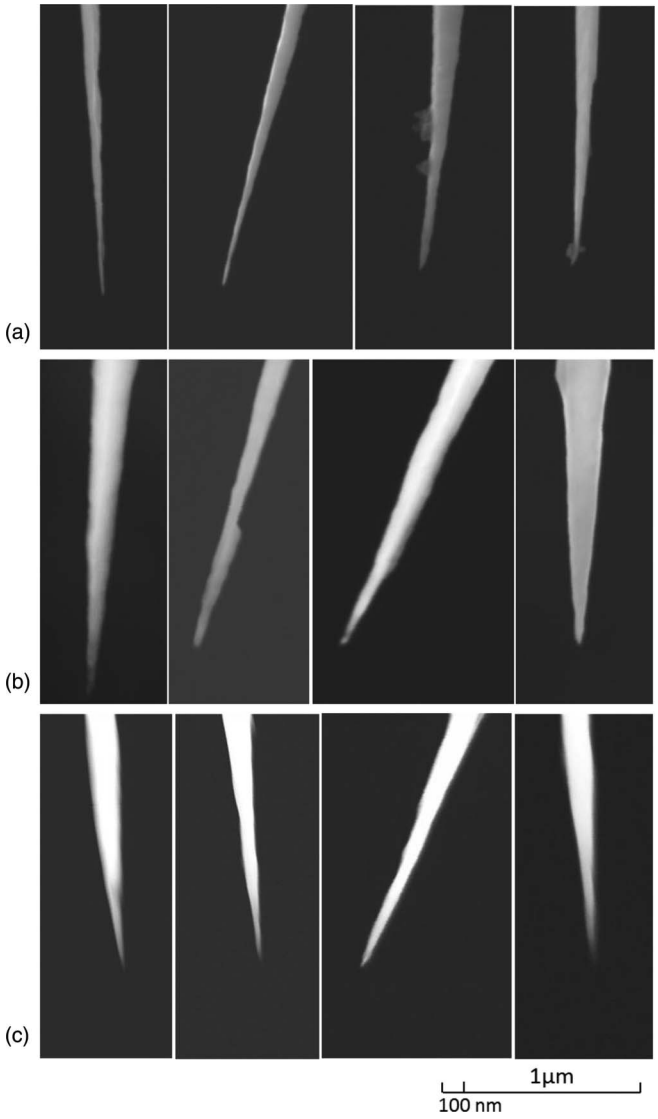

FIG. 8. W tips electrochemically etched following the conditions from Table II, with a CE diameter of (a) 250, (b) 300, and (c) 1000 μm.

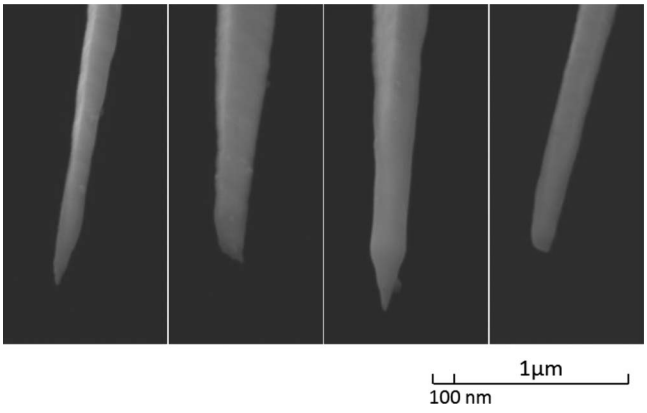

FIG. 9. W etched tips with bad quality, still showing adequate surface morphology and near-nanoscale dimensions.

IV. CONCLUSIONS

A new, simple, electrochemical etching method was successfully developed without requiring any complex apparatus or electronic/mechanical system. By using a power source, an etching unit and a flowing circuit we are able to fabricate high quality tungsten tips suitable for using in application were a needle-type probe is needed to perform an electrical, electrochemical, or mechanical action. Besides the bare wire application, the easily achievable nanoscale miniaturization that this method provides, also simplifies the testing of already existing or newly found materials at the small scale, provided that they can be grown as suitable thin films.

Tungsten wires were easily etched to acquire a pointed shape with sub-micrometric or nanometric tip curvature radius, in less than 60 s, by following simplistic manual procedures. Needle shaped wires with <10 nm radius and high aspect ratio were fabricated in short etching periods of 50 s.

ACKNOWLEDGMENTS

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